

Time-temperature superposition in viscous liquids

Niels Boye Olsen, Tage Christensen, and Jeppe C. Dyre

Department of Mathematics and Physics (IMFUA), Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark

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Dielectric relaxation measurements on supercooled triphenyl phosphite show that at low temperatures time-temperature superposition (TTS) is accurately obeyed for the primary (α) relaxation process. Measurements on 6 other molecular liquids close to the calorimetric glass transition indicate that TTS is linked to an $\omega^{-1/2}$ high-frequency decay of the α loss, while the loss peak width is nonuniversal.

Liquids approaching the calorimetric glass transition have very high viscosities and very long average relaxation times compared to, e.g., room-temperature water. The study of highly viscous liquids is fascinating because – independent of the chemical nature of the intermolecular bonds – these liquids share a number of common features [1–11]. The most significant common features are: i) non-Arrhenius temperature-dependence of the average relaxation time, and ii) non-Debye linear response functions. This paper addresses an old empiricism relating to the latter, *time-temperature superposition* (TTS) [12].

The average relaxation time is basically the time it takes for the liquid structure to relax to equilibrium after a small perturbation. This quantity is easily determined from the frequency-dependence of quantities like dielectric constant [13], specific heat [14,15], shear modulus [16], or bulk modulus [17]. Measurements are usually reported in terms of the frequency-dependence of the response function's imaginary part, the “loss.” The inverse loss peak frequency is a measure of the average relaxation time [18].

When temperature is lowered any loss peak moves towards lower frequencies. This is a rather dramatic effect in the sense that a temperature-change of just a few percent of the calorimetric glass transition temperature T_g usually changes the loss peak frequency by more than one decade.

Loss peaks are often plotted in log-log plots. If the shape of the loss peak in this plot is temperature-independent the liquid obeys TTS with respect to the response function in question $\chi(\omega)$. Mathematically, if T is temperature and $\tau(T)$ the average relaxation time TTS is obeyed whenever functions N and ϕ exist such that $\chi(\omega, T) = N(T)\phi[\omega\tau(T)]$. The factor $N(T)$ is usually a weak function of temperature.

When TTS applies response functions are easily measured over many decades of frequency. This is done by combining measurements done at different temperatures. This procedure works even if only one or two decades of

frequency are directly accessible (as in, e.g., mechanical relaxation probed by the torsion pendulum technique or some of the first ac specific heat measurements [15]). Clearly, TTS is extremely useful if it is correct. But is this the case?

TTS has a long history [19]. For many years TTS was assumed uncritically and used extensively. As accuracy increased and frequency ranges widened, more and more systems were found not obeying TTS. It turned out that TTS-violations were not just exceptions but, in fact, quite common. These violations were initially explained as being due to interference from an additional minor relaxation processes, the so-called β relaxation often found at frequencies higher than those of the α relaxation. Several problems remained, however. From a practical point of view, if TTS does not always work it cannot be assumed *a priori*. Thus the option of constructing wide-frequency master curves was no longer available. Also, additional relaxation processes may always be postulated to “explain” TTS-violations, but what is to be learned from this?

In this situation the nonpolymeric scientific community became skeptical of TTS (for polymers TTS is still often assumed [20]). For several years now there has been little interest in TTS for nonpolymeric viscous liquids close T_g . In the less viscous regime at higher temperatures where mode-coupling theory is believed to apply, this theory's TTS-prediction has received some confirmation from both experiment [21] and computer simulations [22]. From the mode-coupling perspective, breakdowns of TTS in the very high viscosity regime correlate with the well-known breakdown of ideal mode-coupling theory here.

We are mainly interested in the behavior of [equilibrium] highly viscous liquids just above T_g . If TTS is general this would give an important input to theory. Similarly, connecting TTS to other features of the relaxation would also be important. Our motivation for reinvestigating the validity of TTS close to T_g is the following. Dielectric relaxation often exhibits a high-frequency tail a few decades above the α peak, known as the Nagel wing. The Nagel wing is temperature-dependent and plays an important role in TTS-violations [23,24]. Although generally thought to be part of the α process [23,25], it has recently been suggested that the Nagel wing instead derives from an additional, partly hidden β process [26–28]. A few months ago this was confirmed by long-time annealing experiments on propylene carbonate and glycerol by Schneider, Brand, Lunkenheimer and Loidl [29] (for glycerol β relaxation was reported at high pressures long

time ago [30]). The obvious question now is: What happens at temperatures low enough that any influence of β relaxation is eliminated – is it possible that α relaxation does obey TTS after all?

Our dielectric set-up, which is briefly described in Ref. [31], covers frequencies from 1 mHz to 1 MHz. The dielectric loss is determined with a precision better than 10^{-4} . The absolute temperature uncertainty is below 0.1 K with relative variations during a frequency sweep below 1 mK [32].

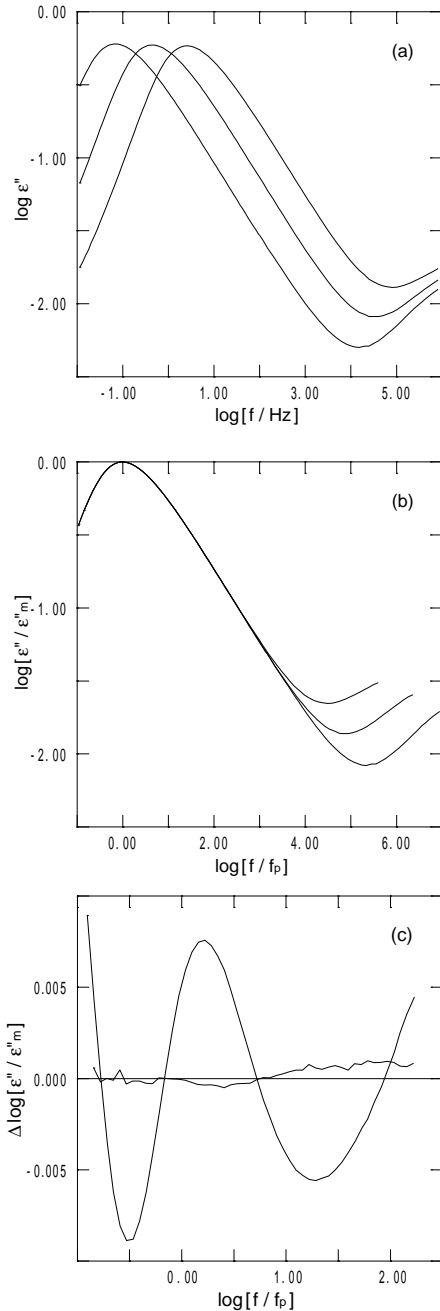


FIG. 1. Time-temperature superposition (TTS) for dielectric relaxation of triphenyl phosphite. To avoid the “glassy” phase [33] the liquid was cooled fast to 210 K. (a) Log-log plot [base 10] of the dielectric loss (imaginary part of dielectric constant) as a function of frequency f at 206.0, 208.0, and 210.0 K. As temperature is lowered the loss curve is displaced towards lower frequencies. The figure gives raw data (16 points per frequency decade); below 10 mHz the loss increases due to a DC contribution [not shown]. (b) Same data scaled by the maximum loss ϵ_m'' on the y-axis and by the loss peak frequency f_p on the x-axis. TTS is obeyed at low frequencies but violated at high frequencies where β relaxation sets in. (c) Detailed test of TTS. The noisy curve gives the difference between the curves in (b) at 206.0 and 208.0 K, the sinusoidal curve gives the difference between the 206.0 K curve in (b) and its best Havriliak-Negami fit.

Figure 1 shows the dielectric loss for triphenyl phosphite [Aldrich, 97%]. Figure 1a gives the raw data, Fig. 1b shows the same data scaled to check TTS. Visually, TTS is obeyed. A closer look is provided by Fig. 1c which compares the difference [noisy curve] between two curves of Fig. 1b to the difference [sinusoidal curve] between one curve and its best Havriliak-Negami fit [34,35]. We conclude that TTS is obeyed quite well. In fact, deviations are roughly as expected from the 1 mK temperature inaccuracy.

For triphenyl phosphite α and β relaxations are unusually well separated. This is because the β peak is at higher frequencies than for most other viscous liquids. Two things are to be noted from Fig. 1. First, TTS applies for the α relaxation whenever temperature is low enough that β relaxation does not interfere. Secondly, the high-frequency slope of the α peak is close to $-1/2$. How general are these findings? Is TTS universally obeyed whenever additional relaxations do not interfere? Is the high-frequency α slope close to $-1/2$ whenever TTS is obeyed? These questions are looked into in Fig. 2.

Figure 2a shows how α peak widths vary with temperature for triphenyl phosphite (\bullet) and 6 other molecular liquids. This is done [23] by giving w , the logarithm of the width at half maximum relative to a Debye process, as a function of loss peak frequency – the latter quantity providing a convenient measure of temperature. When TTS is obeyed w is temperature-independent. Most liquids seem to converge to TTS at low temperatures (the same is seen in the data of Nagel and coworkers from 1990 [23]), but this is not without exceptions. In these cases (e.g., glycerol) TTS may be violated because of interference from additional relaxations, but it shall be hard to prove this.

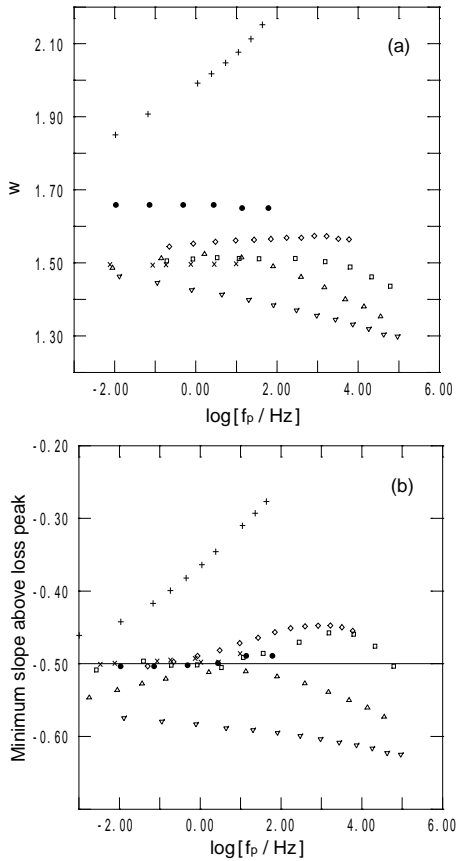


FIG. 2. Loss peak width and exponent of approximate high frequency power-law for α relaxations as functions of \log [base 10] of the loss peak frequency f_p . The abscissa is a convenient measure of temperature with low temperatures to the left and high to the right. (a) Loss peak width w defined by $w = W/W_D$, where W is the width at half maximum in the log-log plot and W_D is the same quantity for a Debye relaxation process [23]. When TTS is obeyed w is temperature-independent. This happens for some, but not all, liquids at low temperatures. Data are shown for the following liquids: Triphenyl phosphite [97%] (\bullet), pyridine-toluene solution [31] (+), tripropylene glycol [97%] (\diamond), dipropylene glycol [techn.] (\triangle), dibutyl phthalate [Sigma, unspecified purity] (\square), diethyl phthalate [$>99\%$] (\times), glycerol [$>99\%$] (∇). (b) Minimum slope above the loss peak of the dielectric loss (in log-log plot) for the same 7 liquids. A comparison with (a) shows that the minimum slope is close to $-1/2$ whenever TTS is obeyed.

How about the α loss peaks for the liquids that obey TTS, do they have anything in common? Clearly, the width is nonuniversal. If the α process follows a high-frequency power-law the exponent may be estimated by evaluating the minimum slope above the loss peak in the log-log plot. Figure 2b shows this minimum slope for the same 7 liquids. Comparing with Fig. 2a we find that the minimum slope is close to $-1/2$ whenever w is virtually temperature-independent.

Figures 2a and 2b suggest that for many liquids TTS is obeyed at sufficiently low temperatures and that, when-

ever this happens, the α loss decays as $\omega^{-1/2}$ at high frequencies [36]. We have indications that this picture applies also for the frequency-dependent shear modulus [37,38] (which we can measure between 1 mHz and 50 kHz [39]), but the shear data are more noisy than the dielectric data.

To conclude – generalizing the triphenyl phosphite observations – we find that

- TTS is often obeyed for the α relaxation at low temperatures [40].
- Whenever this happens the α loss decays as $\omega^{-1/2}$ at high frequencies.
- The α loss peak width is nonuniversal.

An extension of this is the following conjecture:

- There is always a β relaxation [41], though it is sometimes hidden under the α process and only visible as a Nagel wing.
- Whenever temperature is so low that additional relaxations do not interfere, the α relaxation obeys TTS.

To prove this beyond any reasonable doubt, however, one would have to improve sensitivity at ultra-low frequencies and, for some liquids, measure over many years.

To some extent the above 3+2 points reflect the opinion prevailing in this research field 30 years ago, now generally regarded as obsolete. Thus, Johari and Goldstein originally conjectured that β relaxation is “a characteristic property of the liquid in or near the glassy state” [41]. In this situation, of course, any TTS-violation gets a logical explanation since α and β relaxations have quite different temperature-dependencies [42]. The $\omega^{-1/2}$ high-frequency α peak decay was also in focus at that time and several theories were proposed to explain this [43].

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